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A > Carboxyl group-containing diene rubbers*FIELD OF THE INVENTION*

The present invention provides rubber mixtures which contain a diene rubber with a concentration of carboxyl groups of 0.1 to 2 wt.% and a glass transition temperature of -120 to -50° and their mixtures with fillers, optionally other rubbers and rubber auxiliary substances and vulcanisates prepared therefrom. Rubber mixtures according to the invention are suitable for producing highly reinforced, abrasion-resistant moulded items, in particular for producing tire treads which have particularly high wet skidding resistance and abrasion resistance and a low rolling resistance and also for tire sidewalls with especially high fatigue resistance.

BACKGROUND OF THE INVENTION

Double bond-containing anionic polymerised solution rubbers, such as solution polybutadiene and solution styrene/butadiene rubbers, have advantages over the corresponding emulsion rubbers when producing low rolling resistance tire treads. The advantages are based, inter alia, on the ability to control the vinyl content and the glass transition temperature and molecular branching associated therewith. Particular advantages in relation to the wet skidding resistance and rolling resistance of the tires result therefrom in a practical application. Thus, US-A 5 227 425 describes the production of tire treads from a solution SBR rubber and silica. To further improve the properties, numerous methods for modifying the end groups have been developed, as is described in EP-A 334 042, with dimethylaminopropyl-acrylamide or, as described in EP-A 447 066, with silyl ethers. However, due to the high molecular weight of the rubber, the proportion by weight of the end group is small and can therefore have only a small effect on the interaction between filler and rubber molecule. Inter alia, the present invention is intended to provide diene rubbers with a much higher concentration of effective groups for interacting with fillers and with a particularly low glass transition temperature.

US-A 2 662 874 describes the preparation of elastic materials from metal ion cross-linked polymeric carboxylates with a concentration of 0.001 to 0.3 carboxyl equiva-

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lents per 100 g of rubber. The elastic materials mentioned have a very wide range of carboxyl group contents and are unsuitable for the tire application in the present invention due to the inherent sensitivity to hydrolysis of the metal salts.

5 A process for preparing carboxyl group-containing (3.9 to 8.9 wt.% of carboxyl groups) solution polybutadiene rubbers is described, inter alia, in DE-OS 2 653 144. These rubbers have glass transition temperatures which are too high ($> -50^{\circ}\text{C}$) due to the high concentration of vinyl and carboxyl groups and are associated with disadvantageous damping properties and are therefore not a substitute for 1,4-polybutadiene rubber in tire treads and tire sidewalls.

SUMMARY OF THE INVENTION

Therefore the present invention was intended to provide mixtures of carboxyl group-containing solution rubbers from which tires with improved wet skidding resistance, lower rolling resistance and high mechanical strength and improved abrasion behaviour can be produced.

The present invention therefore provides rubber mixtures containing one or more rubbers with a concentration of bonded carboxyl groups or their salts in the range 0.1 to 2 wt.% and with a glass transition temperature in the range -120 to -50°C and one or more fillers in the range 10 to 500 parts by wt. with respect to 100 parts by wt. of rubber.

Preferred rubber mixtures according to the invention are those in which the carboxyl group-containing rubber has a concentration of bonded carboxyl groups or their salts of 0.1 to 1 wt.% and a glass transition temperature in the range -120 to -50°C , preferably -120 to -70°C and a concentration of 1,2-bonded diolefins (vinyl content) in the range 0 to 50 wt.%, in particular 1 to 15 wt.% and a cis-1,4-content in the range 30 to 100 wt.%, in particular preferably 90 to 100 wt.% and also has an average molecular weight (number average) of 50 000 to 2 000 000, preferably 100 000 to 1 000 000 and Mooney viscosities ML 1+4 (100°C) of 10 to 200, preferably 30 to 150.

The glass transition temperature can be determined using known methods, e.g. by using DSC (differential scanning calorimetry, rate of heating 20 K/min). The concentration of carboxyl groups can also be determined using known methods such as e.g. titration of the free acid, spectroscopy, elemental analysis, etc.

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Rubbers according to the invention for use in rubber mixtures according to the invention can be prepared preferably by polymerisation using coordination catalysts or by anionic solution polymerisation. Coordination catalysts in this connection are understood to be Ziegler-Natta catalysts, coordination catalysts and monometallic catalyst systems. Coordination catalysts are preferably those based on Ni, Co, Ti or Nd. Catalysts for anionic solution polymerisation are based on alkali or alkaline earth metals such as e.g. n-butyllithium. In addition, known randomised control agents for the microstructure of the polymer may be used. These types of solution polymerisations are known and are described e.g. in I. Franta *Elastomers and Rubber Compounding Materials*; Elsevier 1989, pages 113 - 131 and in Houben-Weyl, *Methoden der Organischen Chemie*, Thieme Verlag, Stuttgart, 1961, vol. XIV/1 pages 645 to 673 or in vol. E20 (1987), pages 114 to 134 and pages 134 to 153.

The diolefins used according to the invention for polymerisation are 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-vinyl-1,3-butadiene and/or 1,3-hexadiene. 1,3-butadiene and isoprene are particularly preferably used.

The carboxyl groups may be introduced into the rubber either by adding carboxyl-providing compounds, for example CO₂, to metalised solution rubbers or by treating the final rubber with carboxyl group-containing compounds, for example carboxyl group-containing mercaptans, in a subsequent reaction.

The carboxyl groups are preferably introduced into the rubber after polymerisation of the monomers being used in solution by reacting the polymer obtained, optionally in the presence of radical starters, with carboxylmercaptans of the formula (I)



in which

5 R^1 represents a linear, branched or cyclic $\text{C}_1\text{-C}_{36}$ alkylene group, which may optionally be substituted with up to 3 further carboxyl groups, or which may be interrupted by nitrogen, oxygen or sulfur atoms or a $\text{C}_6\text{-C}_{12}$ -arylene group,

and

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X represents hydrogen or a metal or ammonium ion.

This process is a further subject of the invention.

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$\text{C}_1\text{-C}_{36}$ alkylene groups are understood to be any linear, cyclic or branched alkylene groups with 1 to 36 carbon atoms which are known to a person skilled in the art, such as methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, t-butylene, n-pentylene, i-pentylene, neo-pentylene, n-hexylene, cyclohexylene, i-hexylene, heptylene, octylene, nonylene, decylene, undecylene and dodecylene.

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Preferred carboxylmercaptans of the formula (I) are thioglycollic acid, 2-mercaptopropionic acid (thiolactic acid), 3-mercaptopropionic acid, 4-mercaptobutyric acid, mercaptoundecanoic acid, mercaptooctadecanoic acid, 2-mercaptosuccinic acid and their alkali and alkaline earth metal or ammonium salts.

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3-mercaptopropionic acid, mercaptobutyric acid, 2-mercaptosuccinic acid 2- and 4-mercaptobenzoic acid and their lithium, sodium, potassium, magnesium, calcium or ammonium salts are particularly preferred. 3-mercaptopropionic acid and its lithium, sodium, potassium, magnesium, calcium or ammonium salts are more particularly preferred.

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In general, reaction of the carboxylmercaptans with the solution rubbers is performed in a solvent, for example hydrocarbons such as pentane, hexane, cyclohexane, benzene and/or toluene, at temperatures of 40 to 150°C in the presence of radical starters, e.g. peroxides such as dilauroyl peroxide, azo-initiators such as azobisisobutyronitrile, benzopinacolsilyl ethers or in the presence of photo-initiators and visible or UV light. Preferred radical starters are diacyl peroxides such as dilauroyl peroxide, didodecanoyl peroxide, di-(3,5,5-trimethylhexanoyl) peroxide and perketals such as 1,1-di-(tert.-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di-(tert.-butylperoxy)-cyclohexane and 1,1-di-(tert.-butylperoxy)-butane.

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The amount of carboxylmercaptans to be used is governed by the concentration of bonded carboxyl groups or their salts required in the solution rubber being used in the rubber mixtures.

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The carboxylate salts may also be prepared after introduction of the carboxylic acids groups into the rubber, by neutralising them.

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Suitable fillers for rubber mixtures according to the invention are any fillers which are known to be used in the rubber industry, these including both active and inactive fillers.

The following may be mentioned:

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- highly disperse silicas prepared e.g. by precipitation from solutions of silicates or by flame hydrolysis of silicon halides with specific surface areas of 5 - 1000, preferably 20 - 400, m²/g (BET surface area) and with primary particle sizes of 10 - 400 nm. The silicas may also optionally be present as mixed oxides with other metal oxides such as Al, Mg, Ca, Ba, Zn, Zr or Ti oxides;

- synthetic silicates such as aluminium silicate or alkaline earth metal silicates such as magnesium silicate or calcium silicate, with BET surface areas of 20 - 400 m²/g and primary particle diameters of 10 - 400 nm;
- 5 - natural silicates such as kaolin and other naturally occurring silicas;
- glass fibre and glass fibre products (mats, ropes) or glass microbeads;
- metal oxides such as zinc oxide, calcium oxide, magnesium oxide, aluminium oxide;
- metal carbonates such as magnesium carbonate, calcium carbonate, zinc carbonate;
- 10 - metal hydroxides such as e.g. aluminium hydroxide, magnesium hydroxide;
- carbon blacks. The carbon blacks to be used here are prepared by the lamp black, furnace black or channel black processes and have BET surface areas of 20 - 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks;
- 15 - rubber gels, in particular those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene.
- 20 Highly disperse silicas and/or carbon blacks are preferably used as fillers.

The fillers mentioned may be used individually or as a mixture. In a particularly preferred embodiment, the rubber mixtures contain a mixture of pale-coloured fillers, such as highly disperse silicas, and carbon blacks, as filler, wherein the mixing ratio of pale-coloured fillers to carbon blacks is 0.05 to 20, preferably 0.1 to 10.

The fillers are then used in amounts in the range 10 to 500 parts by wt., with respect to 100 parts by wt. of rubber. 20 to 200 parts by wt. are preferably used.

Rubber mixtures according to the invention may contain, in addition to one, two, three or more different carboxyl group-containing solution rubbers according to the invention, other rubbers such as natural rubber or also other synthetic rubbers.

5 Preferred synthetic rubbers are described, for example, in W. Hoffmann, Kautschuk-technologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Compounding Materials, Elsevier, Amsterdam, 1989. They include, inter alia,

	BR	polybutadiene
10	ABR	butadiene/C ₁ -C ₄ -alkyl acrylate copolymers
	CR	polychloroprene
	IR	polyisoprene
	SBR	styrene/butadiene copolymers with styrene contents of 1-60, preferably 20-50 wt. %
15	IIR	isobutylene/isoprene copolymers
	NBR	butadiene/acrylonitrile copolymers with acrylonitrile contents of 5-60, preferably 10-40 wt. %
	HNBR	partially hydrogenated or fully hydrogenated NBR rubber
	EPDM	ethylene/propylene/diene copolymers

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and mixtures of these rubbers. For producing vehicle tires, natural rubber, emulsion SBR and solution SBR rubbers with a glass transition temperature above -50°C, which may optionally be modified with silyl ethers or other functional groups, e.g. according to EP-A 447 066, polybutadiene rubber with a high 1,4-cis content (>90
25 %), which has been prepared using catalysts based on Ni, Co, Ti or Nd, and polybutadiene rubber with a vinyl content of up to 75 % and their mixtures are of particular interest.

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Rubber mixtures which are quite specifically preferred according to the invention contain, in addition to one or more carboxyl group-containing rubbers with a glass transition temperature between -110° and -50°C, additional rubbers chosen from the

group consisting of natural rubber, polyisoprene and styrene/butadiene copolymers with styrene contents between 10 and 50 wt.%. The amount of these additional rubbers is usually in the range 0.5 to 95, preferably 40 - 90 wt.%, with respect to the entire amount of rubber in the rubber mixture. The amount of these additionally added rubbers is again governed by the particular intended use of the rubber mixtures according to the invention.

Obviously, rubber mixtures according to the invention may also contain other rubber auxiliary substances which are used, for example, to cross-link the vulcanisates produced from the rubber mixtures or which improve the physical properties of the vulcanisates produced from rubber mixtures according to the invention for a specific ultimate use.

Sulfur or sulfur-providing compounds, and also radical-providing cross-linking agents such as organic peroxides may be used, for example, as cross-linking agents. Sulfur is preferably used as a cross-linking agent. In addition, as mentioned above, rubber mixtures according to the invention may contain further auxiliary substances such as known reaction accelerators, antioxidants, thermal stabilisers, light stabilisers, anti-ozonants, processing aids, plasticisers, tackifiers, blowing agents, colorants, pigments, waxes, extenders, organic acids, delaying agents, metal oxides and activators.

The rubber auxiliary substances according to the invention are used in conventionally disclosed amounts, wherein the amount used is governed by the later ultimate use of the rubber mixtures. Amounts of rubber auxiliary substances in the range 2 to 70 parts by wt., with respect to 100 parts by wt. of rubber, are, for example, conventionally used.

In the case of rubber mixtures according to the invention which are filled with highly active silicas, the use of additional filler activators is particularly advantageous. Preferred filler activators are sulfur-containing silyl ethers, in particular bis-(tri-

alkyloxysilyl-alkyl)-polysulfides, as are described in DE 2 141 159 and DE 2 255 577. In addition, oligomers and/or polymers of sulfur-containing silyl ethers corresponding to the description in DE 4 435 311 and EP 670 347 are also suitable. Mercaptoalkyltrialkoxysilanes, in particular mercaptopropyltriethoxysilane and thio-
5 cyanatoalkyl silyl ethers (see DE 19 544 469) may also be used. The filler activators are used in conventional amounts, i.e. in amounts of 0.1 to 15 parts by wt., with respect to 100 parts by wt. of rubber.

Rubber mixtures according to the invention may be prepared, for example, by mixing
10 the carboxyl group-containing solution rubber with the corresponding fillers and optionally further rubbers and further rubber auxiliary substances in appropriate mixing equipment such as compounders, rollers or extruders.

Rubber mixtures according to the invention are preferably prepared by first polymerising the monomers mentioned in solution, introducing the carboxyl groups into
15 the solution rubber and, after completing polymerisation and introduction of the carboxyl groups, mixing the solution rubber in the corresponding solvent with the appropriate fillers and optionally further rubbers and further rubber auxiliary substances, in particular plasticisers, in appropriate amounts, and then removing the solvent with hot water and/or steam at temperatures of 50 to 200°C, preferably under
20 vacuum.

The invention also provides use of the rubber mixtures according to the invention for producing moulded items of all types, in particular for producing tires, especially tire
25 treads and tire sidewalls.

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Examples

Example 1

5 6.25 of 3-mercaptopropionic acid and 1 g of dilauroylperoxide were added to a solu-
tion of 500 g solution polybutadiene rubber, CB 45 NF (Bayer AG, Li-type, cis-1,4-
content about 40%) in 4 l cyclohexane at 80°C. The mixture was then stirred for 7
hours at 80°C. Then 2,5 antioxidant Vulkanox 4020 (Bayer AG) and 101.3 g aro-
10 matic mineral oil Enerthene 1849-1 (BP) were added and the solvent was distilled off
using steam (100-110°C). After drying at 70°C under vacuum, 593 g of rubber ex-
tended with 20 phr mineral oil were obtained. Sulfur content 0.3 wt%, carboxyl group
content 0.5 wt% (based on rubber), viscosity ML 1+4 (100°C) 59, cis-1,4-content
40%, glass transition temperature: -88°C.

15 **Example 2:**

The following rubber mixtures were prepared in a 1.5 l kneader (mixing time 5 min-
utes, ejection temperature 150°C). Sulfur and accelerator were admixed afterwards
on a mill (50°C):

TABLE 1

Comparison 2.A Example 2.1

in the kneader mixed:

Buna VSL 5025-1 (37,5 phr mineral oil extended L-SBR, Bayer AG)

	61,9	61,9
natural rubber	10	10
polybutadiene rubber Buna CB 45 (Bayer)	45	0
carboxylic group containing BR according example 1 (20 phr oil content)	0	54
mineral oil Enerthene 1849-1 (BP)	20	11
silica Vulkasil S (Bayer AG)	70	70
silane Si (69 (Degussa Hüls)	6	6
carbon black Corax N121 (Degussa Hüls)	10	10
zinc oxide	3	3
stearic acid	1	1
protective wax Antilux 654 (Rheinchemie	1,5	1,5
antioxidant Vulkanox HS (Bayer AG)	1	1
antioxidant Vulkanox 4020 (Bayer AG)	1	1

On the mill admixed

N-cyclohexylmercaptobenzthiazolsulfenamide

Vulkacit CZ (Bayer AG)	1,8	1,8
diphenylguanidine Vulkacit D (Bayer AG)	2	2
sulfur	1,5	1,5

The rubber mixtures were subsequently vulcanized at 170°C for 15 minutes. The following vulcanisate properties were obtained.

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	Comparison 2.A	Example 2.1
tensile strength (Mpa)	16,8	18,2
elongation at break (%)	450	330
modulus at 100%	2,4	2,9
modulus at 300% elongation (Mpa)	9,5	16,3
rebound elasticity at 70°C (%)	54	63
hardness (shore A)	66	66
tan delta at 70°C	0,138	0,108

The experimental data confirm the significant lower dynamic damping at 70°C, measured by rebound elasticity and tan delta, which in practice correlates with a significantly reduced rolling resistance in tires.

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Example 3:

Preparing a masterbatch from precipitated silica and carboxyl group-containing BR rubber:

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Using the method in example 1, 500 g of BR rubber Buna CB 65 in 4 l of cyclohexane at 80°C were reacted with 12.5 g of 3-mercaptopropionic acid and 0,5 g of dilauryl peroxide. Reaction time: 5 hours. At this point 36% of the 3-mercaptopropionic acid had reacted. The carboxyl group content of the polymer was 0.38 wt.%. Then, with stirring at 75°C, 2.5 g of stabiliser Vulkanox® 4020 (Bayer AG), 189.5 g of aromatic mineral oil Renopal® 450 (Fuchs Mineralölwerke) and 405 g of highly active precipitated silica Vulkasil® S (N₂ surface area about 180 m²/g, Bayer AG) were added and the mixture was stirred for about 30 minutes at this temperature until these components were uniformly distributed. The solvent was then removed by passing steam (100-110°C) through the mixture. The reaction vessel was heated to 75-80°C from outside during this procedure. Finally, the moist solid was removed, finely divided silica was filtered off through a sieve, and the product was dried at 65°C under

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vacuum. 1090 g of a brown silica/rubber masterbatch (99 % of theoretical) were obtained. The waste water contained no silica.

Comparison example 3.A:

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The same procedure was used as described in example 3, wherein a solution of 500 g of BR rubber Buna CB 65 and 2.5 g of Vulkanox[®] 4020 in 4 l of cyclohexane were mixed at 75°C with 400 g of highly active silica Vulkasil[®] S. The solvent was then removed by passing steam (100-110°C) through the mixture, wherein the reaction vessel was heated to 75-80°C from outside. Finally, the moist solid was removed, finely divided silica was filtered off through a sieve and the product was then dried at 65°C under vacuum. 597 g (66 % of theoretical) of an inhomogeneous silica/rubber masterbatch were obtained. The waste water contained large amounts (about 75 % of the amount used) of silica.

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